The Journal of the
American Leather Chemists Association

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PANEL DISCUSSION
on
LEATHER MAKING

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Fifty-fourth Annual Meeting
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The program of the ALCA Fifty-fourth Annual Meeting, held in the New Ocean House, Swampscott, Massachusetts, from May 25 through May 28, 1958, included on the last morning a lively panel discussion on leather-making. Dr. Robert Stubbings, vice chairman of the Convention Committee, opened the session and immediately turned the discussion over to Dr. Reuben G. Henrich, B. D. Eisendrath Company, who acted as chairman and moderator. Dr. Henrich described the formation of the panel and introduced the members: J. Thomas Chain, Diamond Alkali Company; Alfred G. Fleisch, Pfister-Vogel Tanning Company; E. Daniel Lord, J. S. Barnet & Sons; and Dr. Frank W. Panepinto, Wm. Amer Company.

Dr. Henrich explained that the 1956 Symposium on Chrome Tanning sponsored at the ALCA Fifty-second Annual Meeting by the combined Tanners' Production Clubs of the United States and Canada had been of such importance and interest that the ALCA Council had decided to devote the present discussion again to chrome tanning.

LEATHER MAKING

CHAIRMAN HENRICH: We thought it might be well to start our discussion with the preparation of chrome tanning liquors. In order to get the discussion going, I am going to ask Mr. Chain to say a few words about the preparation of chrome liquors.

MR. CHAIN: Most of the tans used in this country are made by a combination of sodium bichromate, sulfuric acid, and sugar. There are various ways of combining these ingredients to make the tan. The first is to mix sodium bichromate and acid and reduce it by adding sugar. The second would be by mixing chrome and sugar together, and adding acid. The third would be by mixing acid and sugar, and adding bichromate.

Of these three methods it would appear that the best is to add sulfuric acid to the sodium bichromate and then add sugar. This type of tan comes to cationic equilibrium rapidly, whereas the other methods take considerable time, which means a storage problem in the tannery to let them age until they gain equilibrium. In 24 hours you will get approximately a 100% cationic tan by mixing tan, acid, and sugar. The others will take anywhere from a week to four months. Eventually they will approach each other if you age them long enough, but this is not too practical in the tannery.

There is also some discussion as to the temperature at which you should reduce the chrome. When you reduce and hold the temperature down below the reflux conditions, you will end up with a higher amount of organic material, and you are not too sure what it is—mostly oxalates—, and you reduce the basicity. So if you want to reduce the chrome cold, it will be necessary to add alkali to arrive at the same basicity as you do if you reduce it hot.

C. DAVID WILSON (Fred Rueping Leather Company, Fond du Lac, Wisconsin): A reduction can be made at the highest possible temperature—that is, within a degree or so of the boiling point of water—and I suggest to you that that is the easiest to control; that is, it is always at 99° or 100°C. It is the easiest to control, but I would like to know whether it makes the best leather.

MR. LORD: I believe that the way you make it depends on what you do and how you use it. I agree with Mr. Wilson that if you reduce the tan hot and concentrated, you can reproduce your results much closer from time to time. If you reduce it more dilute or colder, it is difficult, unless you have complex equipment, to maintain the exact rate of oxidation and reduction, and to maintain the equivalent temperature from time to time. If you reduce as hot as you can and as quickly as possible, at least you should have a start toward uniformity.

A further point that should be considered is concentration. For instance, if you were to make your tan at a concentration of a pound of bichromate in a gallon, or at two pounds to the gallon, you would undoubtedly obtain a slightly different result in each case. On the other hand, I think either one of these would be comparable from time to time and would analyze similarly. At least, that has been our experience.

ADAM M. LAMMERT (Chemtan Company, Port Washington, New York): Would there be any difference in a liquor which has been reduced very slowly—naturally, I would like to say, where we work so slowly that we never reach a temperature higher than we want to reach—and a liquor in which we keep the temperature down, through a cooling coil, at the same temperature as we want to use? Would there be a difference in the liquor between the two methods? The first one is reducing it slowly so that our temperature never will get out of control. The next one is where we have a cooling coil in the reduction vessel and cool it down and hold the temperature down artificially, but keep on going with our reduction.

MR. LORD: Your question is difficult to answer because there is a difference between the two methods. If you reduce slow enough so that your temperature never gets hot, it never gets hot in any part of the solution. On the other hand, even with cooling coils, it is still possible to lose volatile materials from the hot part of the solution, although the average temperature is reduced by cooling.

Maybe Dr. Stubbings can answer Mr. Lammert's question.

DR. STUBBINGS: We don't know. We have run it in the laboratories by cooling inside and by trying to keep the temperature cool from the outside—ice-bath-type of thing, or water-bath. But the real question is the one Mr. Wilson mentioned: What type of leather do you get by using these different liquors?

If it can be definitely shown that a certain type of liquor produces a certain effect on your leather, then it is worthwhile worrying about the necessary controls to produce that type of liquor.

Our work has been entirely in terms of the chemical nature of the reduction—laboratory work. Here we can show definite differences between the different types of reduction. But how much this affects the leather, we don't know.

DR. PANEPINTO: I think if we are following the usual course of chemical reaction, certainly we are going to have different products in both cases. Because reaction rates, concentrations, and so forth, and temperature, always have an effect on the products of reaction. Therefore, I would doubt very

much—although I have not had too much experience with the reduction—whether the products you get at or near the boiling point would be the same type of product that you would get with a cooling coil, as Mr. Lammert suggested. Therefore, it would require a lot of experimental work in both cases. You would have a terrific range of experiments.

MR. FLEISCH: More or less to supplement what Dr. Panepinto said—we have found within our reduction unit that we would have 20°F. difference from one part in the reduction tank to the other part, which would indicate, as he said, that it would be quite difficult to keep the reaction temperature low. In other words, you are getting a localized action, even if it is still hot.

We tried several years ago keeping our temperature down to 165°F., rather than letting it go to our usual 212° or 214°. And I would say that we could not see too much difference in the resultant leather caused by that cold-prepared liquor. As a matter of fact, it was a little bit looser, and yet I don't know that that is conclusive. I feel the same as Mr. Wilson, that I would like to have more of an expression of opinion from people in the audience, if anybody has done anything along those lines.

MR. WILSON: Let's be specific: Which makes the firmer leather?

MR. CHAIN: I will guess: the one with the low organic material.

MR. WILSON: And low temperature?

MR. CHAIN: Yes.

MR. FLEISCH: That being the case, would it not be smart to try to keep the temperature down?

MR. CHAIN: It is not too practical. I really think if we could write down the ideal material—"x" amount of chrome, "y" degree of basicity, and "q" percent of formic or oxalics—then maybe we would have a chance to make a chrome liquor that would fall into that formula. But it would be a brave man in this room who would stand up and say exactly what this compound should be. At least I am not going to say it.

CHAIRMAN HENRICH: Mr. Thorstensen, have you comments along that line?

EDWARD THORSTENSEN (S. B. Foot Tanning Company, Red Wing, Minnesota): I may have a few thoughts, but I don't think I will have very many comments.

The question that has been asked is a very interesting one, and I think if you will go back into some of the work that was done under the direction of Dr. Theis not too many years ago, you will find answers to a lot of these questions. I was party to running about 30 tests, and if we had started where we ended up, we would have found the answer right away instead of doing all of the work. But then we would still have been wondering what would have happened had it been done some other way.

You will find in Dr. Theis's work that the answer you are looking for here is "in answering, what are the effects of the degradation products of sugar or glucose, or what have you?"

Personally—and this is purely a personal opinion—I do not believe in reducing at the maximum temperature. I believe the reduction should be controlled not by trying to keep the temperature down artificailly but by extending the time over which you enter your reducing agent. In that way you retain most of the degradation products of sugar. I agree that you will get softer leather. But again, you can control this. The hotter you reduce, the more you drive off the degradation products in the form of gases of many kinds, and for that reason you have a stack over your reducing tank. But if that stack is just there to take away the things you don't want, plus the excess heat, I think you will find a liquor that will give you a nice round piece of leather without having hard spots in it. You make use of the sugar itself—that is, the products of degradation—in building up your leather, instead of just looking for the chrome to tan your leather.

CHAIRMAN HENRICH: I would like to ask one question on that: Why not reduce with sulfur dioxide, then, instead of glucose, and add the organics that you want? Has anybody comments along that line?

MR. CHAIN: Can we ask what organic you will want and add?

MR. FLEISCH: And how much?

DR. THEODORE D. BRAUNSCHWEIG (Loewengart & Company, Mercersburg Tannery Division, Mercersburg, Pennsylvania): I did quite a bit of work many years back on various types of reducing liquors. We did reduce sodium bichromate with SO_2 and found this was a very beneficial pretanning liquor for the type of leather we wanted at that time. It holds the leather flat, and at that time we made patent leather and wanted a very smooth and flat grain, and we found that the SO_2-reduced liquor was more convenient for this purpose.

We also made a reduction by first adding the glucose to the bichromate and then reducing with sulfuric acid. By running the glucose in the sulfuric acid–bichromate mixture, we found entirely different liquors. The reduction

which was done by adding the sulfuric acid to the glucose-bichromate mixture gave us a much higher masked chrome and less filling. But the one where the glucose was added last had more filling. So for pretanning we used two liquors: SO_2-reduced liquor for the patent leather, and the glucose-reduced liquor for other types of chrome leather. And the liquor where the glucose was added last was used for filling. Temperature at boiling point gave us an easier control, but we definitely lost filling characteristics of the chrome liquor.

Now, Stiasny did tremendous work on this in the years 1925 and later, and there are a lot of analytical reports on the various types of liquors produced. If somebody will take the trouble of going back to this work, he will find a lot of answers to the questions which have been raised here.

MR. LORD: I would like to ask one point: The Doctor said when he reduced them hot, he lost filling properties. There are three things: sulfuric acid, chrome, and sugar. The sulfuric acid and chrome are fixed, because we definitely have in mind the ratio we want. Now, the thing that is not fixed is the amount of sugar and glucose that we add. Would it not be true that if you lost some of that with, say, 25% the amount of glucose that you have of chrome—if you lost some of that when boiling hot, could you not compensate by using more sugar and get more filling?

DR. BRAUNSCHWEIG: It is true that if you add more sugar you get more filling, but by reducing at a lower temperature and not running this through a smokestack—it is a waste of material to first run it through the smokestack and then add to the liquor something that you had there before.

MR. LORD: But isn't most of your filling due to your sugar as such? Or is it due to the organic or volatile acids that you lost? Do volatile acids actually give you much filling?

DR. BRAUNSCHWEIG: Now this is just an opinion, and I have no analytical basis for what I am saying. But I believe that at lower and higher temperatures different organic products are formed which we do not know. At least I don't know them. But the products which are formed during these various types of reduction have an effect on the leather. I have no doubt about that.

MR. KLEIN (Wells Chemical Company): Don't you feel that there is a possibility of the variation in the salt content having an effect on the filling action of the chrome solution that is used? In other words, you can attain a certain physical effect with the concentration of the salt.

MR. LORD: When you say "salt", do you mean sodium chloride?

MR. KLEIN: Yes.

DR. PANEPINTO: I might be able to answer that. At our tannery we are using a most unusual process in that, although it is two-bath, we seldom have to get rid of our chrome solutions. We merely add what is needed. According to the literature, that should not be; the type of leather will be too flat, and the salt concentration or salt build-up will be such that the leather will not be salable.

Actually, we change our chrome liquors maybe once a year and maybe twice a year. And the only reason it is done then is because it is dirty due to the skins that have gone in there from the bate.

We both pickle and tan simultaneously in the same solution, and every day we analyze our liquors, bring our volume to a given value, and merely replace the dichromate and hydrochloric acid that are required.

However, I tried the same thing at another tannery, a goatskin tannery, where the specialty was India goatskins; after the third try—after replacing the dichromate and the hydrochloric acid—after the third pack had been put in, the sorters could immediately tell the difference in the leather.

So there you are. That was my experience, and still is. So that salt concentration apparently in the case of goatskins does not seem to matter very much, and there must be a terrific build-up.

BEN A. GROTA, JR. (Fred Rueping Leather Company): What did the sorters see?

DR. PANEPINTO: The leather began to be open and flat. The grain would pebble. That is what we are getting now. But the process is such that the mechanical stages through which the leather goes will compensate for that, and we end up with approximately the same kind of leather. Actually, we are probably getting a different kind but compensating through the mechanical stages.

FRANK ZEISSIG (Hiteman Leather Company): Do you think you could compensate for this condition in the beamhouse or by adding a little masking agent to tan?

DR. PANEPINTO: You mean in the bate?

MR. ZEISSIG: Yes.

DR. PANEPINTO: The difference was this: In the other tannery—it was the old Burk Tannery—we did it the old way. We used the two-bath lime, the old lime and new lime. We used the new bate and the old bate. Then

we used the two-bath chrome. Do you notice everything was in two's? The leather would go from one bath to the other. And then after it was taken out of the second or the old lime, it was put in the new lime, and then from the old bate into the new bate, and then into the pickle, and finally into the two-bath chrome.

Something must have happened during that period which would probably be analogous to what Mr. Adam Lammert and others have mentioned—the slow process of making something. Therefore, you would not expect to get the same kind of result that you would if the process were run very quickly. As you mentioned, Mr. Zeissig, there was a possibility of doing it that way, but we never followed it up.

CHAIRMAN HEINRICH: I realize that liming, bating, and all these things play a part and are definitely interrelated. But I think we must consider that our stock has been properly prepared for chrome tanning. We do not want to get back to liming and bating.

One comment on this condition that Dr. Panepinto was talking about: I think that where they do that, the salt concentration builds up to a certain point after a few days, and after that it does not vary. You take out as much as you put in.

DR. PANEPINTO: I agree.

DR. HENRY B. MERRILL (B. D. Eisendrath Tanning Company): Going back to the chrome liquors, I would like to ask a question. When you mix the dichromate and acid, and then add an excess of sugar, part of the sugar is completely destroyed (going up as carbon dioxide), part is converted into organic acid, and if you add enough sugar, part of it remains as unaltered glucose (or as dextrin if you are using corn syrup). Does the unaltered gluclose or dextrin play any part in tanning? Does it create fullness, or is it simply inert? And if it does create greater fullness, how does it do it?

DR. H. G. TURLEY (Rohm & Haas Company): That is one way to get moldy leather—and then you go ahead and put antiseptics on top, a backward motion.

On the question of sugar, it seems characteristic of the tanning industry to take a reaction and, with this so-called art and skill, to carry it out in as many ways as you can think of.

Surely for controlled chrome tanning there would be nothing better than a reduction of bichromate to chromium sulfate, and to adjust your basicity to what you find suits you, so that you have no excess of reducing agents.

There has been a lot of talk about the organic acids, but I am not aware

that there has been much work done in identifying them. The only acid we ever found was oxalic acid.

When you leave sugar in, you do improve one effect: You raise the precipitation point of the chrome so that the tan can be run at a distinctly higher pH before the chrome precipitates. That may be a mixed blessing; it is not always good. To some extent there is a hindering or a masking of the chrome.

Since I am sure it is impossible with excess sugar to control this reduction absolutely, because you get varying quantities of residual sugar and salt, it is a bad idea. If you must have the effect of these materials, it is always better to put them in afterwards; then you can make a choice. As you know, the literature covers dozens and dozens of so-called masking agents.

In the sense that the sugar enables you to tan with a less-precipitating tannage, I think the tanners can to some extent make a little fuller leather—run it at a little higher pH without getting into trouble. It is surely better to do it the other way around: to have a more or less straightforward chrome liquor, adjust the fullness by the prior treatments, and by the quantity, and the extent of the basicity of the chrome. That is the way we feel about certain reduced liquorsl

MR. CHAIN: If you have a little free sugar in your prepared tan, as sugar or glucose, by the time you tan the leather and shave it and rinse it for an hour or so, how much free sugar is left in the leather then? There is some free glucose in most of these tans, but by the time you tan the leather and analyze it, how much is there? If there is no way for it to combine with the skin, it just washes out.

DR. PANEPINTO: As to the last remarks of Dr. Turley, does the reduction of sugar or any ingredient have the same effect as having a reduction of that same ingredient under the conditions that we are dealing with? The reason I say that is this: Some are still using lump lime with arsenic. If the arsenic is put in the lump lime during the slaking, you get an entirely different effect than if it is put in after the lime is hydrated.

MR. CHAIN: If you make a chrome liquor with no sodium sulfate in it and add the same amount of sodium sulfate that you get out of the normal chrome liquor (about 25%), you don't get the same thing. Just adding salt as salt is not the same as making a tan liquor that has salt in it as a result of a reaction.

In my experience, if you take a chrome that has no salt and add salt to it, you will get less chrome take-out. It reduces the amount of chrome that goes on the leather. That is not what you get when you build the sulfate into the tan.

CHAIRMAN HENRICH: When you are adding glucose, and if you are adding an excess, how far can you go before the excess glucose has no effect whatsoever? Is there a point in there where you are just wasting material?

MR. CHAIN: If nothing else, you get an awful lot of foam you don't know what to do with.

MR. LORD: There is another effect we should consider: The hygroscopic effect of sugar helps in the shaving room. Everybody has trouble with leather drying out in the shaving room. If you have that small amount of excess sugar in the skins, and have edges that dry out, they wet-back better.

There is a gentleman here who can tell us about sodium sulfate in tans: Mr. Axelrad of Fiber Chemical.

F. F. AXELRAD (Fiber Chemical Corporation): I am not a practical tanner and can't contribute much, but we did find that more chrome goes on the fiber if you have no salt in chrome liquor.

We did some investigating to find out what kind of tanning you have if you start with a pure basic chromium sulfate. We tried to investigate what the addition of various salts will do to changing the tanning effect, what quantities will be optimum, and which type of salt will produce the best results.

We started with pure basic chromium sulfate and investigated the ratio of chrome to salt, and we found that if you have no salt present, more chrome goes on the fiber. And sometimes it is un-uniform. So we have to find out how much salt we have to add to have a uniform tanning effect. This is as far as we have gone.

MR. LORD: When we chrome tan a piece of leather, we have in mind more than one thing. We are not interested in just chrome tanning. We have an interest in what that skin looks like on the sorting table. There is no question that a lot of that character is determined in the chrome bath.

What I would like to hear in discussion is this: How do we add to produce the smoothest type of leather, if we are producing a grain leather? What produces the smoothest grain with the finest pores, particularly in the calfskins we are looking for today?

DR. BRAUNSCHWEIG: If it is only a question of producing the smoothest grain, according to my personal experience any oxalato mask of chrome will produce that effect.

MR. LORD: I mean smoothness with everything else, as well as plumpness.

Dr. Braunschweig: Varic s speakers here have asked: "What is the best chrome?" or "What is the best leather?" I don't think there is such an animal. Because when we make leather, we try to make a product which expresses a certain character which we think from our point of view and in the interest of our customers is the thing we are looking for. It is a personal thing, to a certain extent, and representative of our company. And our competitors express themselves by their know-how and by their operations in a different form and produce leather of different characteristics. And as happens with leather, some people prefer one, and some another. But within the same factory, we also make various types of leather for various purposes. Handbag leather requires different characteristics from shoe leather. Billfold leather has different characteristics. So there is no such thing as talking about the "best" for the "best." We can only say that if we want to have this end product, then it is advisable to perform such and such operations and to use such and such material.

So when we discuss chrome tanning, we can only stick more or less to basic facts like the fact that liquor made under such and such conditions will have such and such characteristics while leather made under different conditions will have different characteristics. We have to find out for ourselves whether this type of liquor will bring out the characteristics in the leather which we are producing.

Mr. Lord: I think actually what we mean, in words of two syllables, is that some people want to make shrunken leather and some people want to make smooth.

[*Laughter*]

Lester M. Whitmore (Leas & McVitty, Inc.): When you are talking about excess sugar in the chrome liquor, what magnitude are you talking about—50% excess or 25% excess?

Mr. Lord: I think most people who make chrome liquors don't know how much excess sugar they are using. I know formulas which call for 100 lb. of bichromate of soda and from 25 to 50 lb. of sugar. In either case there is an excess when you figure it theoretically. However, when you try to reduce chrome practically with a theoretical amount of sugar, you run into difficulties.

Dr. Turley: There is no doubt that with low basicity and a simple liquor, you get a smoother grain and flatter leather. You plump it according to the way you raise the basicity and pH and so forth, and with masking agents.

A very interesting way of chrome tanning which I have known about for quite a few years is to utilize that principle. So in this chrome tanning a

portion of it—perhaps 25%—is given to the skins first, at a low basicity range and low salt concentration. That gives already a smooth grain. When the grain is tanned, therefore, it will better resist changing. If this is followed by possibly 50% of chrome at a higher basicity to take care of the internal fibers, you can achieve the ideal or come near it—the ideal being to get the smoothness of a 5 to 7 or 9 to 12 calfskin and yet have all the plumpness.

You can also see how this is arrived at by taking a low-basicity chrome. During the course of neutralization or setting, which goes on slowly, there is, first of all, fixation at low basicity; then neutralization goes on inside the skin.

If there is lime left in the skin, that will automatically do the same thing but in a different way. However, if you take a uniform-equilibirum pickle and go along with your setting, you can achieve a uniform result.

I think having chromes of different basicities is a clever way of tanning.

Mr. Lord: You say that if you first use a liquor with a relatively low basicity on your pickled stock, you will tan the grain first and will fix the grain so that when you put more basic tan on, you will have it smoother. That may be right theoretically, but unfortunately it is difficult to tan the grain first under those conditions. If you make a cross section of the leather, you will find that the grain is still not tanned and has to wait for the basic solutions to get a tan under those conditions. You have more or less an equilibrium set up in the leather when you use an acid tan on top of the pickle. The grain does not tan.

Dr. Turley: I have to disagree with you on that. If you use a limited amount of chrome tan—an insufficient amount—, it won't tan the leather completely. If you put on too much of the chrome, it will go through the leather.

Mr. Lord: Suppose we have an equilibrium pickle of about 2.25 pH and we put on an acid tan. What pH will the tan that we put on have—3 or lower?

Dr. Turley: Let's not assume that. Let's assume we will pickle with a tan having a pH of about 3.5.

Mr. Lord: On the other hand, when you are talking about an equilibrium range of 3.5 pH in the pickle—well, maybe somebody does it.

Dr. Turley: It is being done.

Mr. Zeissig: We have been talking about the effect of Glauber salt and sugars in the tan. I would like to ask whether any of you have any data on the relative merits of all these agents—the effects from the amount of salt

of Glauber salt? Are there any practical data or information on the differences caused by these additives?

MR. CHAIN: I think three or four people here have more data than we have on the relative merits of formates, phthalates, and whatnot. It is their business.

MR. ZEISSIG: I mean sugar, salt, and Glauber salt.

MR. CHAIN: You mean in a prepared tan—whether you have 25% sodium sulfate against 15?

MR. ZEISSIG: Yes.

MR. CHAIN: I am sorry. I don't have any information on that.

CHAIRMAN HENRICH: Mr. Zeissig, don't you have any comments on starting your tan with low-basicity liquor and ending up with a high one?

MR. ZEISSIG: We do start with a low-basicity liquor, and then a higher one, and finally a still higher one. It is practically a neutralization by tan liquors.

CHAIRMAN HENRICH: Do you find it gives you better results?

MR. ZEISSIG: In our particular case, it does, yes.

CHAIRMAN HENRICH: Has anybody any comments with regard to salts and glucose in tanning liquor?

ANDREW SALAMATOV (Barrett & Company): If I may be excused, I think we are running in circles. I don't believe that there is any such thing as the best chrome liquor, just as there is no such thing as the best leather. Every tanner thinks he makes the best leather in the world. That is what I hear from everybody. Now, it is not just a question as to how you prepare your chrome liquor but rather how you prepare a liquor and how you can keep that liquor constant for your particular use. Once you get that, you are free to do almost anything with it, because there are so many intangibles and so many variables in usage of the chrome liquors—just as many probably as in preparation, and maybe more. So I don't believe it is so important as to how the chrome liquor is prepared. What is important is how a prepared liquor can be stabilized for use in a given factory; and once stabilized, what will be the best procedure to be adopted to produce the desired results.

Now, are we still making tan liquors, or are we tanning leather?

CHAIRMAN HENRICH: We are starting to tan leather, let's say.

MR. SALAMATOV: From the point of view, now, of using the tan liquor to obtain the desired results, I think some very tangible things are important. And among them I think things like dilution or concentration, rate of addition, temperature, level of salt, and so forth, all affect the leather. But I think we are losing ourselves in trying to say which chrome liquor is better, and whether or not less sugar or more sugar will make a better leather.

MR. WILSON: Are you willing to spend a couple more minutes on preparation? There is one other thing I would like to talk about. Almost every tanner has been approached by manufacturers of glucose regarding the quality of the glucose that is used. And from the cost standpoint it makes a great deal of difference which quality is used. The Rueping Company uses probably the most expensive glucose it can buy—a 43° Baumé glucose. I am not sure why we do. I would like to have somebody tell us why we use the expensive glucose.

Can we talk a little about lower qualities of reductants—that is, technical sugars, for example, or even, if someone has had experience with it, about molasses?

MR. CHAIN: As chrome tan producers we are interested in reducing costs like everybody else, but we are not able successfully to use black strap molasses, which is the bottom of the ladder. There are too many impurities; you have foaming troubles. So it has been our experience that you are ahead in the long run to use a good grade of sugar.

MR. WILSON: I would say that has been our experience, too, but I don't know anything about the qualities of leather that would be produced by the lower-quality sugars.

DR. MERRILL: We do not use the best grade of corn syrup. We have been approached by a representative of one of the glucose companies who has urged us to use a grade in which hydrolysis has been carried out to a little greater extent, so that the product contains more reducing sugars and less dextrins. Our attitude has been that it does not make much difference whether the corn syrup is a little more or a little less hydrolyzed when received, since when it is added to a highly acid and hot material, hydrolysis must take place very rapidly. The difference in cost is insignificant, incidentally.

I have visited tanneries which are making excellent leather, where they were doing part of the reduction by adding leather shavings. We have at

times experimented with liquors—and they worked all right—where we used lignosulfonates for part of the reduction—not for all of the reduction. We did the bulk of the reduction with lignosulfonates and then finished up with gluclose.

I can agree, though, that it would not be desirable to use highly impure material, so that some of the impurities would actually be in the liquor.

DR. PANEPINTO: Would you say that you can adapt yourself to any type of product of that kind to suit your purposes—the particular leather you are making?

DR. MERRILL: I hardly know how to answer that. Actually the cost of the reductant is very small when you consider the total cost of making leather. Recently we had occasion to compare two types of leather, and we found that the difference in cost between one type of liquor and another type was about 25 cents for a pack of 2,000 lb. of skins. That is not very much. We think it is better to use a reasonably good grade of corn syrup which is constant in composition and bought from a reliable company, and that small savings by using cheaper materials probably would have little or no effect on our balance sheet.

CHAIRMAN HENRICH: I am wondering if Mr. Hirsch from Trostel has any comment on this problem of glucose reduction of liquors.

ARTHUR HIRSCH (Albert Trostel & Sons Company): We reduce by running the acid into the bichromate sugar solution, and we get the effect which we expect and want—the plumping effect in the leather.

CHAIRMAN HENRICH: How about the quality of the glucose? Do you find that you can use any type?

MR. HIRSCH: We haven't made any changes, so I have had no chance to compare.

MR. ZEISSIG: I think probably a better grade of glucose would be more dependable and would meet specifications a lot easier than a poorer grade. It would come up to specifications more consistently.

DR. PANEPINTO: Could you adjust your process to accommodate a lower-grade glucose?

MR. ZEISSIG: You probably could, but I still think the better grade would vary least from batch to batch. In the long run it would be more dependable.

MR. KLEIN: Assuming everything is the same, such as the dichromate-acid ratio prior to reduction of the sugar, has anybody any experience not with the grade of sugar but the type of sugar to produce a certain type of leather? Starting with dextrose and sucrose and glucose? Is there an effect on plumping depending on the type of sugar, or is there a filling action?

Some people prefer mixtures. I know one person who likes to reduce entirely with sucrose. What has been the experience of others as to the type of sugar rather than the grade of sugar?

DR. PANEPINTO: Before sucrose could do any reducing, it would have to be changed to the glucose type; then the reactions would be similar to glucose.

MR. KLEIN: I would go along with that to a point, but I am wondering if we don't get a higher type of molecular masking agent. Or would it be possible? In other words, the degradation products would not be of the lower types of formates but of the higher types, and would be those possessing more side chains.

CHESTER A. ROSS (Ohio Leather Company): To get back to a point made about foaming, I think that is one reason we probably use a good grade of glucose. We have tried several different kinds of inferior grades, and foaming seems to give us the biggest problem. Maybe we added our glucose a little fast, but we have investigated black strap molasses, shavings, and so forth. We don't think that the cost is great enough to warrant a change, so we use the best grade of glucose.

MR. LORD: When we make a chrome liquor, and the reduction is complete, and we cool it off, how soon are we going to use that liquor? We know that liquor ages. We know that more of the free acid present at the beginning actually combines with the chrome and that as the liquor ages, it becomes higher in pH. This is very noticeable.

When you make a chrome liquor, then, are you going to let it stand for a period of time before use? If you buy a prepared tan, you have a material that has been dried out and aged to its maximum extent, and that is one of the biggest differences between making the tan yourself and buying a prepared tan.

When we reduce our own chrome, for any given ratio of sulfuric acid to chrome there is a decided difference in pH in the liquor.

MR. CHAIN: Our pH is all the same.

MR. LORD: That is the most amazing thing. He says that regardless of what basicity they make their chrome, the pH is about the same. It is

really surprising, because there is a decided difference in the ratio of sulfuric acid to bichromate of soda.

DR. TURLEY: I don't think it is amazing, because you are again dealing with small quantities, and over that pH range the change in pH is very small, as we all know; yet the qualitative difference in the amount of acid is considerably larger. I don't think it is surprising.

MR. LORD: Maybe it is not surprising as far as prepared tan is concerned. But if you make, say, two tans, and make one up with a ratio of 80 parts of sulfuric acid to 100 chrome and make another up with equal parts of acid and chrome, and measure the pH of that solution for a month, you will find that they are not the same and don't even approach the same point.

DR. TURLEY: What are the differences?

MR. LORD: After aging for three or four weeks there will be a difference of at least a quarter of a pH point.

DR. TURLEY: . . .which is small.

MR. LORD: Of course, and the one with the least acid to begin with maintains a higher pH.

DR. TURLEY: That is a small change.

MR. LORD: A change of a quarter pH in a liquor that you add to your wheel is a large difference, I think.

DR. TURLEY: I never thought our industry would get to the point where a quarter of a pH would be of great significance. I am glad to see it. The quantitative ratio of acid to base is significant, and you don't pick it up easily by measuring pH.

DR. BRAUNSCHWEIG: Whether the difference of a quarter of a unit in pH is important or not for tannage is for the individual manufacturer to decide. However, the changes which take place in the chrome liquor are significant and indicate that there are changes in the molecular composition of the chrome; and if your pH changes from the moment you make your chrome, you have a constant change in the pH toward a more acid chrome.

Again, I would like to quote Stiasny's work, because he has made extensive studies on the chrome complex by measuring the variation of the pH

which took place in aging chrome liquors. I don't have the information in my head, but it is certainly in his book and in his papers.

CHAIRMAN HENRICH: Maybe somebody here has had some experience whereby they prepared two chrome liquors, supposedly exactly the same, one of them aged for a day or so before it was used, and another that stood for a period of time. What differences did you find in your leather?

CLIFFORD BENRUD: We don't like to use new liquor, but after liquor is aged for three days we don't find any particular difference.

MR. GROTA: What differences do you see in the leather?

MR. LORD: The differences we notice are that in order to bring out our leather at the point we want, we have to use more bicarbonate in one place than the other.

DR. SALAMATOV: So what?

[*Laughter*]

WENDELL MORRIS (Consultant, Grand Haven, Michigan): Speaking of olation, I would like to quote something that George McLaughlin once said—that olation is important and noticing it is important, but the difference of adjustment of a blade of one thousandth of an inch will make still more difference.

MR. ZEISSIG: Mr. Lord's statement that you have to use more bicarbonate in one case or less in the other is important. If you want a smooth piece of leather, less will help. The least amount required is a step in the right direction. I think Mr. Lord has an important point when he speaks about getting a different over-all effect in tanning by using less bicarbonate.

ZYGMUNT PANZER (Sandoz, Ltd., of Canada): In our tannery we ran some loads with tans that were only one day old and some with tans that were a few days old. Now, we were not particularly looking for any changes in the leather, but we could not notice any differences. The pH of the prepared liquor varied from 0.1 to 0.2 pH; however, the end pH of the tan was always the same. It is possible that it was due to the masking agent that was added during the tanning operation.

MR. ZEISSIG: Getting back to the pH and the use of more or less bicarbonate—we ran some suede tests using varying amounts of bicarbonate in

neutralizing. If we went up too high in bicarbonate, our leather flattened out, and we lost a lot of our plumpness. So I don't think you can say that it makes too much difference whether you add 0.5%, 0.25%, 0.75%, or 2%.

Dr. Panepinto: It not only does make a difference, but also what alkali you use for neutralizing—whether it is borax, caustic, or bicarbonate. Each of them will produce its own effect.

Mr. Zeissig: These tests were run using the same alkali.

Mr. Chain: If you should tan with freshly prepared liquor, so that you have 70% cationics, 20% anionics, and 10% nonionics, would that liquor dye and fatliquor the same way as if it had 90% cationics?

James Kelly (Ellithorp Tanning Company): When trying to duplicate sugar-reduced chrome liquors by addition of complexing organic material to SO_2-reduced liquors, can anyone here tell me how long after the addition of an organic compound the bulk of the equilibrium will be completed?

Dr. Braunschweig: It is a matter of temperature. If you add your organic masking agents at a high temperature, then you have a very rapid conversion, particularly if the molecular size of the agent is smaller. So if you add a sodium formate, you have practically an immediate conversion. If you use oxalate, it is a little slower; and with phthalate it takes still longer.

Chariman Henrich: We all know that in preparation of these liquors and in some of the commercial prepared materials, we arrive at different basicities. I would like to ask Mr. Chain to comment as to what effect various basicities might have in our tannage and on the leather as far as grain is concerned—or whether they have any effect at all.

Mr. Chain: The efficiency of a tan liquor is dependent on the over-all basicity of the system after you apply the chrome. That is, the over-all basicity includes the acid from the pickle which reduces the basicity.

On light leather such as sheep and goat and calf we seem to get very good penetration with even the highest-basicity chrome that you can get. On real heavy sides you can see a difference in the rate of penetration between high basic tan and low basic tan.

I agree with Dr. Turley that the right way to set chrome is to set it with a high basic tan and eliminate the use of the alkali. Actually, most of the effect of the alkali is that you are just basifying the tan liquor. That is what you put the alkali on there for—to raise the basicity up to around 40.

While I work for an alkali company, I think the less alkali you use the better off you are.

DR. PANEPINTO: Isn't it a fact that if you wash the leather, you will find that after a few hours your shrink temperature rises? So you may not need that much alkali. After the first few hours there is a further rise in shrink temperature, although the rate is not as large as in the first few hours. I found that experimentally on large packs.

CHAIRMAN HENRICH: How about comments from the floor as to basicity and its effect on your leather?

MR. KELLY: It almost seems to be a normal procedure for certain kinds of leather, like drawn grain, to take the most astringent form of tannage. And as long as the penetration and tanning action are there, it works to your advantage.

MR. CHAIN: I think the drawn grain from a high basic tan is caused when you add the alkali. If you use a high basic tan and do not add alkali, the grain will be about as smooth as when you use a low basic tan.

MR. KELLY: I was thinking of using a high-basicity chrome.

MR. FLEISCH: It seems to me that people in side leather are going to higher and higher basic chrome liquors. I know that we have. It may be that we completely changed our tannage at the time, but I do know other people have also gone to higher basic chromes. And no one seems to be able to tell us why. We know the effect we got, but I can't pin it down and say that higher basicity did it, or whether it was the entire pickle and tan that did it.

I must agree with Dr. Turley again that the less alkali you use at the end, the better off you are.

I remember two years ago when he made a point of pH at the end, taking your liquid pH. Dan made a statement about less bicarbonate or more bicarbonate. If you add more or less, and leave it another twenty minutes, what effect will it have on the leather?

Now, in calfskins there may be a different story. But I have found in our tannage that when we come into the tannage with a good lime streak present—about a third of the thickness—our pH never gets lower inside that leather and never gets higher. We stay with a pH of about 3.1, plus or minus one point, on the inside of the leather.

But why should any difference occur? We are able to maintain it in the leather, but not in the liquid by one point.

Now that we have the liquid prepared, what are the effects on the leathers?

Mr. Zeissig: I think a lot of us have found that if we add a quarter or a half percent of bicarbonate at a time for adjustments of the pH of the liquor the leather is changing in that time. If it is added in small doses, it is different than if it is added all at once and run a definite length of time. When added in small doses the running time is longer, which makes a difference. I don't think it is just the acid coming out of the skin.

Chairman Henrich: What is the effect on your final leather?

Mr. Zeissig: The leather, I think, in most cases is looser. You get a poorer break, and it is not as full if you add it in small doses.

Dr. Panepinto: To complicate the picture a little further, if you add acetate instead of carbonate, you will find the finished leather is softer.

We want to keep in mind that what the individual is talking about happens to be the leather with which he has had a lot of experience. Mine happens to be goatskin. It is a little bit of a thin thing, and our process is much more heavy, if you want to call it that, than for leathers such as side leathers and calf. Because we have to get all our chemicals, all our solutions, through that hard, thin skin.

I found that in neutralizing a tan with bicarbonate or acetate or borax, that the finish—the softness, if you want to call it that, the mildness of the leather—is in that direction: it is harshest with bicarbonate, less with acetate, and the least with borax.

Mr. Zinkowsky (Dowdy Dyestuffs Company): We are discussing bacisity here. In going through the trade, I note one thing: that we have the increased use of masking agents of the organic types. We do find enormous differences in these tanneries in coloring, where they play with higher percentages of formate. The basicity of chrome is brought into the picture there. But I wonder if anybody has made a study as to where the basicity winds up after you start kicking it around with these organic masking agents. Because in coloring—getting back to alkali use—where you have a good solid pickle and then run in with your chrome basicities and use the alkalis, we have more difficulty in obtaining an even color. We get a more level coloring job where we don't kick it around so much with the neutralization steps with use of the alkalis. Possibly this is due to the uncontrolled or controlled washing which may vary in many tanneries.

Does anybody have any comments on the result of the masking agents versus basicity in final effects? This will further confuse the issue.

Harold Bernard (G. Levor & Company): It seems to me that we are using very broad terms to find out just exactly what result we want, and

that the result we get is definitely whether we have an equilibrium of neutralization which is caused more through the use of high-basicity tannage or chrome liquors, rather than to try to surface-neutralize, which happens in the case of bicarbonate or the various snowflake sodas—whereby the effect is to neutralize the surface—to overneutralize the surface of the leather, and thereby make the leather coarse or loose by that, rather than to have an equilibrium neutralization which occurs more with high-basicity liquors.

That is the point I feel we are discussing here, and that really occurs in the tanning operation.

Further than that, to go back to the sugar problem, I believe it is better to have 10% too much sugar than to have 1% too little. I think that is the big factor.

MR. SALAMATOV: We are told that chrome liquor, while it is a liquor, is never static. It changes all the time. And it stops changing only when the skins are dried and the chrome begins to be precipitated and set. Now, that being so, I believe that there is always a possibility of obtaining the same result at least by two different methods.

Let me put it this way: The chrome liquor is so complicated that it allows almost an infinite number of variations. I don't know of any other material in the tannery that you can abuse as much as chrome liquor. It may not be the tannage you want, but it still will be some kind of tannage. Now, in order to get the tannage you want, you have to adjust various things, and if it is a matter of adjustment, then there are quite a number of things that can be done.

Let's take basicity. You can get it by preparing a high-basicity liquor; you also can get it by adding some alkalizing agent to your chrome liquor. You can do it by adding a little at a time to the chrome liquor: after every shot of chrome, you can add a shot of alkali and keep your basicity in this way at a point above the prepared liquors. Now, you also can do it by giving the alkali at the end and giving it in small portions or in big portions.

So there are different ways to get similar results. Or rather, I return to my previous statement that is is a matter of adjustment. It is a matter of how to use the liquid which has been in the plant to which you have been accustomed, or which you want to use to produce certain results in leather. No matter how much or how long we talk about this matter, we still have to verify our results on the leather that we make or the leather that we want to make.

Another variant is the use of different alkalis. Mr. Zeissig tells us that there is a big difference between borax and bicarbonate. I remember a couple of years ago that Dr. Merrill told us that when they used borax and bicarbonate for neutralizing on a number of packs—production packs, pack after pack—there was no difference whatsoever found in the leather. So where is the

controlling point, if it is not the leather? How can we say that this chrome liquor will give the best results, if we know that the same results—I don't mean that; I mean: that a given result with chrome liquors, since they are so complex, can be obtained by variations in the methods of preparation or of application or being followed up. My desire is that we try to go into the using of liquors rather than preparing them.

DR. PANEPINTO: Since this is a practical session, we are concerned with the finished product rather than the intermediate products and reactions. There is no doubt that neutralization to a given pH will, in the analytical end, give us the same end result—the same pH. But we are discussing the finished leather.

In my experience, there is no doubt about the fact that by the use of different agents in this particular case—this one item of the neutralizing agent—the finished leather in the eyes of the sorter is different with the various alkalis when that is the only change that has been made in the process.

CHAIRMAN HENRICH: Dr. Merrill, will you comment? We are discussing basicity and the effect on the grain.

DR. MERRILL: I think most people agree that you get the finest grain if you begin your tanning in a rather acid system, which can be accomplished in two different ways: by using a very high pickle and a relatively basic liquor, or by using a somewhat lower pickle and a less basic liquor to begin with.

As has been pointed out, there is an almost infinite number of combinations of degree of pickling, basicity of liquor, masking, and things of that sort, which will accomplish about the same end result.

As far as neutralizing is concerned, it was our experience, as has been remarked, that we saw no difference in the leather whether we used sodium bicarbonate or borax for neutralizing after tanning. I might say that we conducted our tannage in such a way that very little neutralizing was necessary. We have felt that it is best to avoid neutralizing at the end of tannage—or rather, to minimize the neutralizing at the end of tannage. It is our experience that during this neutralizing at the end of tannage most of the additional chrome that is fixed, is fixed on the grain and flesh layers and does impair the smoothness of the grain to some extent. The whole question is complex. That is putting it very mildly.

MR. BENRUD: I would like to ask Dr. Merrill this: Roughly, what is a low pickle pH, and what is a high pickle pH?

Dr. Merrill: Of course it is not altogether a question of pH. It is a question of how long to pickle, too.

I might say we pickle pretty nearly to equilibrium—not wholly. A pH that I would consider low would be anything from a final pH value of 2.5 down.

Talking about smoothness of grain, it is not wholly a question of the basicity of liquor or the pH of pickle; concentration has a lot to do with it.

Some years ago shrunken grain leather became popular. And while it seemed easy enough to get it when you didn't want it, it turned out not to be too easy to get when you did want it.

In one of our early experiments we took a bated skin, not pickled at all, and tanned it in 52% basic liquor at a high concentration. That skin came out about the smoothest skin we ever made. It had some other qualities that were not so good. It was excessively thick. But it did have an extremely smooth grain, probably due to the very high concentration that we used.

Dr. Turley: I think we must regard chrome tanning as a phenomenon—nothing more than that. We are changing the protein collagen to something different. It is still a double-handled chemical. It will still swell in alkalis and acids.

I think we must put our attention on the fibers. We have to keep an eye on the liquors, of course; they are a reflection of what is going on. But we must also keep in mind the quantitative amount of chrome.

Here is a nice question: What would be the difference, let's say, between a 10% low basic chrome and 7% high basic chrome on the leather as to smoothness?

Beyond the basicity of any particular liquor, we also have to consider the quantity and its effect on the plumpness and softness of leather.

I think some of these problems of neutralization are made confusing and complex because of the inattention to time and equilibrium. I have to be careful of what I say, because it depends on the base from which we start. You may draw a grain with 0.5% bicarbonate in the time which you give it—and if you give it longer, there is a beneficial change: the alkali conditions penetrate more into the skin, the grain becomes less alkaline, and that leather becomes smooth again. If you take it out before that time, you will have drawn grain and a tendency to pipiness. If you leave it longer, that will change over.

I think it is one of the advantages of the so-called masking agents that they are a buffering source. You achieve quickly an over-all pH, and because you have an over-all constant or uniform acid or alkaline condition, I think that facilitates dyeing.

The dyeing, again, is another chemical phenomenon and goes on more uniformly if you have a uniform fiber.

We must not forget what I think, after all, is the osmotic condition of the fibers. We have conditions where there is a swelling in the skins. If we depress that swelling with salts operating at a certain pH range, it is the finest thing to do to get smooth and flat leather. That is the finest way to make glove leather. Stretching, the fibers will remain in a horizontal condition, and the grain is the same way—horizontal rather than vertical.

When we get away from that to more acid conditions, then we get into the range where there is more swelling and plumper leather. The masking or buffering agents help us to produce that, and we like that so we can make soft, full, mellow leathers. And if we pay enough attention to the osmotic conditions and salt concentrations, we can make many kinds of crushed grains. There are crushed grains on the market where there are diamonds and squares and high and low valleys. We must pay more attention to the fibers and less attention to liquors, as far as pH is concerned.

MR. ZEISSIG: We talk about equilibirium in all our tanning, but we never really reach that equilibrium. I think in most cases if we did run the stock until we reached equilibirum, we would ruin the fibers mechanically. So we are sort of limited.

In every case there is a partial equilibrium, and that is why the case is so confusing. In the true sense of the word I don't think we ever reach equilibrium in the reaction between the chrome and collagen fiber. It is not a complete reaction—only partial in every case.

MR. LORD: Coming back to what Mr. Zeissig and Dr. Merrill said, that the smoothest leather is made by varying basicity from the more acid tan first, then the intermediate basicity, and finally the more basic type—the smoothest leather is made by not having to add much alkali at the end.

Does it not come to this: that the molecule composed of basic chromium sulfate is much kinder to the leather than when we begin to complicate it with additional agents, like carbonates or borates, which may be astringent, and that the smoothest leather is that produced by basic chromium sulfate?

MR. ZEISSIG: I think everybody tries to keep away from a lot of bicarbonate. At least everyone has said so more or less indirectly, if not directly. I know we are. We are using different basicity tans and keeping our neutralizing to a minimum. I think that is probably true in most cases.

DR. PANEPINTO: While talking about the smoothest leather, we have to be careful about where and what part of the process we are talking about. Is it during the process or in the finished leather? Many of us, I am sure,

can adjust our mechanical operations to give us a fairly smooth-looking leather whereas further back in the process, it may have been a bit harsh.

Dr. Thomas C. Thorstensen (Lowell Technological Institute): It seems to me we have been talking around the subject quite a bit and overemphasizing one point or another.

Dr. Turley has stated that he felt we should place our emphasis upon the fiber. We have also had the statement made that we are dealing with a dynamic system that is changing all the time. And from what is being said as far as practical tanning is concerned, it seems that the least variation, or at least the more mild the changes we make, in our processes, the better off we are.

I think all these things are related. Because we do have in the fiber, as Dr. Turley points out, osmotic effects. We have these changes taking place. There is one fundamental principle in any tanning, as we all know—that the condition of the fiber at the time that the tanning material is fixed, is going to determine the quality or character of that fiber later on. Wetting, drying, or whatever you do, still you tan the fiber in a certain condition. And the condition of that fiber at the time of the tannage is most important.

Now, if we are going to have drastic changes taking place—drastic changes in pH near the end of the process, or heavy lime streaks in the middle, or take a bated skin and hit it with a high-basicity liquor, as Dr. Merrill said—here we are dealing with cases of extreme contrast.

If we bring about our processes more gradually and hold down the swelling or control it, keep pH values fairly uniform, and use mild additions of materials, we should expect to get much smoother leather.

Mr. Fleisch: I agree with Dr. Thorstensen that we should keep our highs and lows in the process at pretty much a common line—cutting down the amount of bicarbonate that is used, as Mr. Zeissig said. We have cut down the amount we have used.

I will talk about bicarbonate (I don't care whether it is borax or anything else—it is the same). If we put in, in one shot, 25 lb. to 7000 lb. of white-weight stock—and that is a small amount to put on that much leather—we are going to get a soft, loose, raggy grain, because we are setting that chrome right on the surface. The pH as we put it in goes away up, and then it starts coming down.

We would rather work from the opposite end to have the higher alkalinity on the inside, and as we approach completion of our tannage, we approach the highest point of our grain pH, the highest in the process. We do use the small amount of bicarbonate to raise that final little bit in the grain, and we don't use too much of it to make the grain loose.

MR. WILSON: I agree with all those who have said that the less neutralizing, the better. However, I do recognize—and I think we all recognize—this factor of smoothness from acidity, and the need for a higher level of, let us say, overall basicity of the leather toward the end of the process.

The question seems to be: How fast do you approach that level? And how do you approach it? We happen to agree with the general philosophy of doing it before you get to the so-called neutralizing step, and to do little or nothing toward the end. Our experience tells us that that produces the tightest-breaking leather, in combination with the smoothest leather.

Somebody made a comparison of bicarbonate and borax. We had one experience that may be interesting to you, although it may be beside the point. If bicarbonate is substituted for borax on a chemical equivalent basis, everything else being equal, the leather is overneutralized. I am not talking about pH's or basicity measurements. I am talking about break, temper, drawnness, and Mullen cap crack.

To be specific, if the chemical equivalent of borax—and again, I am quoting an experience and not stating this as fact, but just an experience—if the chemical equivalent of bicarbonate was substituted for borax, our experience was overneutralization. That is, everything else being equal, there was softer leather, more drawn leather, looser leather, and weaker leather.

If, then, the level of bicarbonate is reduced to a point whereby temper, drawnness, and break are equivalent, the leather is still weaker. Therefore, I agree with Mr. Zeissig that there is a fundamental difference between bicarbonate and borax.

MR. BENRUD: I think it is particularly important that we have our concentrations, our running time, and temperatures so adjusted that we have sufficient tannage before we go into neutralizing. If we don't have these factors under control, the same amount of neutralizing will not always give us the same quality of leather. You may decide, in order to get a higher shrink temperature, that you want to add more of a neutralizing agent. I think you would be far better off if you would run your chrome drum longer or adjust your concentrations so that you would bring up your temperature and get a more thorough tannage before you start neutralizing. In this way you will be able to use less neutralizing agent and come out with a rounder and better-feeling piece of leather.

CHAIRMAN HENRICH: Mr. Benrud, you said, "sufficient tannage" before you start neutralizing. Is there some point where you consider the tannage sufficient, or do you use shrinkage temperature to determine that?

MR. BENRUD: That becomes a matter of practice, again. You will find that if your mill hands float the stock too high or if a valve leaks, the tan

solution will be diluted and your temperatures will not go up. You will not get the degree of tannage, although you may wind up with a higher pH.

DR. PANEPINTO: Each of us is discussing what is happening in our plants—the results of our experiences. I wonder how many have actually taken an inventory of exactly how their process is being run. They are assuming it is being run in a given way. I am speaking from experience of where I went into a plant, went through the entire plant, and found out what each man was doing. But it was not enough. I decided to do it again a few weeks later, and you will be surprised how different things were being run from the first time I was there. I continued that for six months and finally reached the point where they were doing the same thing, and then I wasn't through with them.

However, when I wrote up the process and showed it to my constitutents, they said, "Is that the way we are doing it?" And that has changed over the months and years. But it is surprising how operators will gradually get in the various little ways of doing things, in a shorter way than you told them. They have changed the process around, and you are assuming that it is being run the same way. That is an important point to look to in your own plants.

CHAIRMAN HENRICH: I think that the chrome distribution in the stock plays some part in the final characteristics of leather on the finishing table. I wonder if anybody would like to comment along these lines. I know there are some leathers where the chrome distribution is quite uniform throughout, others in which you have a higher chrome content on the grain and flesh side, and still others where the chrome content is highest in the middle. Let us have comment along those lines.

MR. FLEISCH: As I said before, you can have a high chrome content on the inside of the leather. Our competitors analyze our leathers regularly, as we do theirs, and they could probably tell us more about our leathers than we can tell ourselves.

However, as far as I know, we have a pretty unique chrome curve. Our chrome is quite high on the inside—before splitting—compared to what most other people have. This is probably achieved by the way in which we do our tanning, in that we start our pickle with some of our chrome in it; and whereas we do use the same basicity liquor throughout, by putting the chrome in with the acid, we achieve pretty much a uniform basicity, and that fits in with the statement that we tan on the inside before we tan on the surface.

We have about 40% of our chrome going in with the pickle. We have decidedly more chrome, therefore, fixed on the inside before we start fixing any chrome whatsoever on the grain and flesh. The result is that when we

come along and raise the over-all basicity within the system, we then begin tanning our grain and flesh.

However, we do not, where we keep a low bicarbonate at the end, put in sufficient to have an equilibrium distribution of chrome.

Now, I know good friends of ours who makes lines of leather, and a customer will say, "We will take this one or that one"—and they will have a distinctly opposite chrome curve from what we have. They may use formate, and we don't. Why it should be I don't know. But it just must come down to the fact that elsewhere in our process we have differences that will compensate or that we have to compensate for, so that we make the same type of leather. That is the way ours will work. Our pH is fairly uniform inside and out, coming out of tannage.

CHAIRMAN HENRICH: Do you feel that by doing that, you get a fuller piece of leather with the same over-all chrome content or some of the physical effects that you get? I know it is what you want.

MR. FLEISCH: That is it—it's what we want. We have made that leather that way for years. It is what our customers want. Sure, we have made leathers softer. The trend and tendency is toward softer leathers today, whether it is a combination tan or straight chrome leather. But our leather is about the same as we made it ten years ago, although if we took a leather made ten years ago and put it against a piece today, we might be surprised.

Even though we think we are making the same piece of leather that we did, we might be surprised at what we made ten years ago. We think we are making it, even in our vegetable-tanned leathers. And I don't think there is really too much difference between the leathers even though there is some difference analytically.

ROBERT G. WELDON (Seton Leather Company, Newark): We like to make our leather lively, smooth, and supple. We achieve this by seeking equilibrium conditions wherever we can. Somebody asks how we achieve that. Well, we have a team in our plant, and everybody is a member of the team, and the better trained everybody is, the better you hold your conditions. It is a matter of educating people.

MR. ZEISSIG: In your tanning, if you deliberately ran for two hours instead of a half hour, didn't you change your equilibrium?

MR. WELDON: Yes.

MR. LORD: How much of an exhaustion could we expect to get in a normal chrome-tanned liquor? If we run our tan and adjust it so that we get ex-

cellent pickup—and I won't say what the figures are because I don't know—will our leather be better than if we run it so that our exhaustion of chrome is only partial? Would you say that the leather would be better if some chrome remained in the wheel at completion of the tanning?

MR. ZEISSIG: Yes, I think so. Although it is not economical, I like to see some chrome go down the sewer. I think you get a smoother piece of leather if you do not try to exhaust it completely.

Getting back to the equilibrium business—in a chemical reaction where you add definite quantities and a reaction takes place which is complete, additional quantities of those chemicals will not change the reaction. Our tanning is quite different. There is no such thing as a complete reaction. The reaction is reversible, and can even be changed by longer running time. That is what I think should be stressed.

MR. LORD: That is right. The fixing of chrome depends on a number of things. One is the temperature. As temperature goes up, the fixation of chrome changes the equilibrium. As the temperature goes up, more chrome wants to be fastened on the leather. So there must be some point at which we don't want to go higher in temperature, because we may get too much of a deposition of chrome or a deposition we don't like.

What would you consider the maximum temperature that you should allow a tan wheel to attain at the end of tannage?

ELCANNA PETERSEN (Geilich Tanning Company, Taunton, Massachusetts): There has not been much said about temperatures today, and that is one point that has a lot of bearing on the takeup of chrome.

I know that we had very uneven tanning. Then we changed over all the drums to run at a certain rpm., changed the shelves and the pegs, and found by running the temperature at 103° or 104° that we got a much smoother grain and a good takeup. It gave us the piece of leather we wanted. I think temperature has a lot to do with it. I was able to cut down the amount of bicarbonate also, which had a great effect on the end results.

CHAIRMAN HENRICH: What effect did you find, Mr. Petersen, on the grain in your finished leather?

MR. PETERSEN: I found the grain much smoother and flatter. As we did go up in temperature and tried to have a quick-run chrome, we found that we got quicker tanning, of course, but a much closer grain. But as I said, by lowering our temperatures and the bicarbonate, and with a little longer run, we got a much flatter grain in the finished product.

Dr. Panepinto: I found the same result in the two-bath process, where I reduced with hypo: the lower-temperature hypo gave a smoother and flatter grain. At the higher temperature, the grain was more beady.

Chairman Henrich: May I ask Mr. Fleisch a question: If you had two leathers with the same total amount of Cr_2O_3 in them, and your stratigraphic analysis gave one curve with the high chrome in the middle and the other with low chrome in the middle, what would you expect the difference to be as far as shrink temperature and tear test is concerned?

Mr. Fleisch: As far as shrink temperature is concerned, I can't say I have noticed any difference. Our leather coming out of chrome tannage stands a shrink of 98° to 100° C., and I believe another leather I measured was coming out at a somewhat lower shrink. So I can't say I noticed any differences as far as shrink temperature was concerned.

As far as stitch tear is concerned, I would say the two leathers were quite equal. And that I would have to base on establishing averages over a period of time—our leather against theirs—and also compensating for the difference in thickness. In other words, it should also work on 1" thickness, or something like that, so that you have a comparable thickness rather than taking a 3½-oz. leather against a 5-oz. leather.

But I can't say I found too much difference. That amazed me, because we thought that the more chrome you put in, the stronger the leather would be up to a certain point. We didn't think we had too much in there.

Dr. Braunschweig: I would like to comment on the question of temperature. I think we have been making vague statements, because we should state at what time we measure the temperature. Normally, I would say that a chrome tannage will start out at a temperature of 75° to 80° F., and gradually, as friction in the drum raises the temperature, we will end up with a certain temperature. The temperature at the end of the tannage should have comparatively little effect, if we have at that time a full chrome tannage standing a boil test of 212°. Because at that time if we have a temperature of 103° or 108° or 125°, it does not appear that this should have too big an effect on a leather which stands such a temperature all the way through. If a high temperature occurs in the drum at a time when this high shrink test has not been reached, this surely produces an entirely different type of chrome and not a very desirable one. It becomes rubbery and does not paste right, and when it comes out of the drum, you just feel there is something which is not right. So if we talk about temperature, we surely have to specify at what time we measure it.

Dr. Turley: Continuing Dr. Braunschweig's observations here, I think we have not directed our attention to one of the most important phenomena of chrome tanning. But before I mention that, let me ask a question: How do we know when the chrome tannage is done and you have finished leather? I think a lot of tanners don't know.

The phenomenon that I want to point out is this question of leathering. You start chrome tanning, and it runs for two or three hours, and it is still not the right kind of leather. There is not much difference in the chrome pickup. You reach a certain point, and it is interesting to me to note that some tanners arrive at it on an empirical basis. The common figure could be seven hours.

I was very interested to hear at the Paris meeting of the International Union various tanners—Stanley Briggs, for one—who came out with the same answer, that in about seven hours you had chrome leather. At less than that point, you had something that was not quite as good. What is this phenomenon? When you start neutralizing, what did you have before? Have you produced troubles that you should not have? Something happens here. But there is a certain point at which the fibers change over and become leather. Up to that time, I don't know what you would call them—fibers impregnated with chrome, but not combined with chrome.

I think we ought possibly to have a little discussion on this, because it is a very important point in chrome tanning.

Mr. Zeissig: I think that is a very important point. We tan to a "piece" of leather, and we all have our own specific problems. We may use different basicity tans—a high pickle or a low pickle. When we tan to this "piece", a leather, the end result, will give us a good break, right temper, and the feel we are after.

That is what we tan to, and we try to hold that point or that particular phase. We may call it equilibrium, but it is not really equilibrium. We tan to a certain point, to make a certain "piece" of leather. In other words, we tan to an end result. We find certain conditions will give us the leather that we are after, and we try to hold it. If we change the pickle very much, we are going to go away from it. If we change the running time or the temperatures too much, we will vary too much.

I think it was brought out in one of these meetings that 5° increase in the end temperature in tanning gives a chrome pickup 30% or 40% greater.

I. Leo Riese (Beggs and Cobb, Inc., Winchester, Massachusetts): A year or so ago at a meeting like this, I made a comment about some experiments we had run at our tannery, regarding the effect of temperatures on fixation of chrome. At the time I mentioned that we purposely vary the end temperatures, and we have found that a difference of as much as 7° gave us a

difference of almost 10° in shrink temperature and 0.5% chromium oxide on the dry basis. So that we did find it was very important.

Now, we also found that the time at which you measure the temperature is important. For example, you will not accomplish the same thing if you wait until the tannage presumably is finished, then open the mill and check your temperature, and see instead of 105° that it is only 100°. The book says it should end at 105°.' So take out a couple of barrels of liquor and steam it up for an hour; you still don't get the same effect. You can run it for two hours, in fact, and you end up with the end temperature you want, but you will still not get the same effect.

Apparently the effect of the temperature during the time that the chrome is being fixed before the alkali goes in is the important point. That has been my experience.

MR. SALAMATOV: I think we have come to the point where we begin to talk about what happens in the tanning drum. Now, what do we have in the tanning drum? Acid from the skins which have been pickled, certainly the tanning liquor, some of the sodium sulfate, and probably some of the calcium salt which has been brought with the skins, and we add some salt. And we have different amounts of water.

Now, these are the factors present in every drum, I suppose. We have skins, we have water, we have salt, we have sodium sulfate, we probably have some calcium sulfate. And we have the temperature. Now, we have six or seven variables which we deal with in every tanning room—whether it is Rueping or Barrett or anybody else.

If we can begin to talk about these things that recur from day to day, maybe we can come to certain generalizations. Let us, for instance, say what the effect of dilution is. Suppose you put into a drum ten dozen skins and run them in a given amount of water and salt. Now, instead of using ten dozen skins, say you can put in eight, proportionately reducing the amount of salt and chrome, but leaving the amount of water the same. You have a different dilution. You have a different condition of the chrome liquor. You have a greater ionization. And when the chrome liquor is ionized more, of course it tans a little differently from the concentrated liquor.

What is the influence of this greater dilution or less concentration upon the leather—the end product? Has anybody tried to tan a pack of skins without adding any salt—just pickled skins, chrome liquor, and that is all? I don't think anybody has tried that, and I don't believe anybody will. And it is necessary to know what amount of salt will be effective—whether a 2% solution or a 3% solution, or 4%, or 5%. Who knows? Does anybody?

Now, as to temperature, we just heard that temperature undoubtedly alters the amount of chrome absorbed. But the mere fact that you have more Cr_2O_3 in a skin after it is dried and analyzed—and you have 3½%

instead of 3%—does not give you any reason to jump, because by itself it does not make a better leather. It depends on how the additional chromium was fixed in the skin—whether in the leather or on the grain that will crack later on.

These points I believe are the tangible variables that you can talk about, and I would like to begin to take these variables one at a time.

Let's talk about salt. Has anybody had any experience with varying amounts of salt—whether it is 3% or 4% or 5%? How about dilution? How about temperature?

For my own part, I believe every one of these factors is very important, and I believe by varying just one, you don't get the results that you are after. You have to vary probably one or two more. And then there is always plus or minus. You want to do something to gain on the plus side, but invariably there is always something that happens in spite of you on the minus side. How do you go about those things? This is my idea of having discussion on using the chrome liquor in the drum.

DR. MERRILL: I think everybody knows that the higher the salt concentration, the less chrome you will fix. I don't mean that a very small difference in percentage of salt will have much effect, but I do know if you have a concentration of 6% salt in the chrome liquor, you will fix decidedly less chrome than if you have 4%, other conditions being the same. I think you would fix still more if you had about 2%.

As for the matter of concentration, I do remember that some years ago we tried a species of dry tannage. Our ordinary procedure is to add the chrome tan liquor to our spent pickle liquor and have a float of 100%. What we did was to drain the pickle as much as possible and feed the chrome liquor as a concentrated liquor. We did find that tannage took place a good deal more rapidly and that we could fix the same amount of chrome in the leather by using about two-thirds as much chrome liquor as we normally used, which is something that would be important under wartime conditions or under any conditions of shortage of chrome, but is not very important now.

As far as temperature is concerned, it is perfectly true, as everybody knows, that the higher the temperature, the more chrome you will fix. It is also true that you must be careful of your temperature at the start. I don't think it is necessary, though, to start as low as some people have mentioned. We start our chrome tanning at a temperature of about 85°. In connection with some shrunken-grain work, we have found that about 95° is the highest that we dare go.

We tan at a somewhat higher temperature than some people have mentioned. We go up to perhaps 110°. But that temperature is not reached until the skins have been milled for five or six hours in the chrome liquor.

The temperature, incidentally, is rather difficult to vary in a controlled manner because it depends on the ratio of skin to liquor, the speed of the drum, and to some extent the outside temperature. We attempt to control it somewhat by varying our pickle temperature between summer and winter and by varying the running time in the chrome between summer and winter.

CHAIRMAN HENRICH: Mr. Wilson, any comments as to salt concentration, temperature, and so forth, in your experience?

MR. WILSON: No experience. We add no salts other than those which already exist from the reduction.

CHAIRMAN HENRICH: Dr. Thorstensen?

DR. THOMAS THORSTENSEN: It seems to me that in the question of temperature we must again return to the principle of fiber distortion. If comparatively large quantities of alkali are added at the end of a tannage simply to attain a final pH value, we will have a higher pH on the surface of the leather than in the center. This will result in a swelling differential, a distortion of the fiber, and undesirable grain effects.

If on the other hand we raise the temperature near the end of the tannage in order to fix the chrome, the temperatures inside the skin and outside the skin will be almost identical. The chrome will become fixed without as much fiber distortion. Raising the temperature should then be the safer procedure.

DR. MERRILL: Perhaps I misunderstood, but I thought Mr. Petersen said he got a rougher grain if he used a higher temperature. Am I correct?

MR. PETERSEN: Gentlemen, I get a rougher grain by using a higher temperature. I get the smoother grain by using a lower temperature. Sorry, Dr. Thorstensen, but the customers like it anyway.

MR. FLEISCH: Dr. Thorstensen, I will back you up. We end up with a higher temperature, about 125° on our drums as a day-to-day average.

DR. MERRILL: A considerable part of your production is corrected grain, is it not?

MR. FLEISCH: You are absolutely right—about 20% to 23% of ours is corrected grain.

DR. MERRILL: Isn't it also true with side leather, since so much of it is corrected grain, that an extremely glassy grain is of less importance than to calf tanners?

MR. FLEISCH: That's right. We hope someday to make something as good as the calfskin tanners.

MR. LORD: There is also another part of the chrome tanning subject we have not touched. By varying the chrome tanning, how much can we expect to be able to change the ultimate thickness of our leather? With calfskins today, as you probably all know, the trend is toward plumpness. A calfskin that measures about 12′ and is a thin woman's weight, is a difficult skin to merchandise. You can sell it at a low price to certain women's trade or try to build it up in weight to sell it to somebody who is willing to take an intermediate weight.

Most shoe manufacturers want plump calfskins, and there are not enough of these in the country today to satisfy the demand. How much can we influence the thickness of our finished leather by the chrome tanning? Is it possible by using more chrome, or by changing the method of chroming, to increase the thickness?

I can think of one thing that was brought out a little while ago by Mr. Fleisch. He said that when his skins go into the tan wheel, they have a lime streak in the middle. If his skins have a lime streak in the middle, that piece of leather in the middle should be much thicker than a skin out of the bate that has been bated down to a complete flaccid condition. When the tan is added, it diffuses to the center of the skin and is fixed there fairly rapidly due to the relatively slight acid, or maybe even alkaline, condition.

Is it possible that when he tans his leather this way, he is getting a thicker final tannage than comparable skins tanned on top of an equilibrium pickle, so-called, one where the pH is relatively even through the thickness of that skin? Would there be a difference in thickness of the finished leather?

MR. FLEISCH: I really don't know whether I can answer that. I can make some comments, and I hope when people come to see us that they are not just trying to flatter us. Various people have said they like the feel of the solidity of our leather as it comes out of tannage.

I have never studied it except from the pack point of view. We try to make a plump piece of leather. Most of ours is 5-oz. or better, after splitting and shaving.

DR. MERRILL: What has been said about getting a thicker leather if you do not delime completely is, I think, sound in theory. But for some reason or other, in our experience, it has not worked out in practice.

Last summer I had the privilege of visiting a very prominent German tannery, and I was amazed at two things: first, at the way they handled their stock in the beamhouse and pickle before tanning; second, at how little difference there was between their final product and ours. Their finished

leather was very much like ours in spite of the great difference in beamhouse treatment.

This particular tannery gives a very scant bate and leaves a lime streak in their calfskins that is three-fourths of the thickness of the skin. They give a very superficial pickle, so that the stock going in the chrome liquor still has a pH in the center that must be up around 6 or 7. Then they give an acid tannage, then neutralize, and they come out with a highly regarded leather.

We made some tests using that process or as much of the process as they revealed to me. We had a considerable lime streak when we started chrome tanning. Now, these tests were not made on a very large scale, and they were not made by comparing one side with another but by comparing 100 lb. of skins with another 100 lb. of skins out of the same soak pack. We did not get any increase in weight yield by leaving that lime streak in. Although we should have, we didn't.

J. Buchman (Putnam Chemical Corporation): There are masking agents such as phthalates which will help in deliming and at the same time will also mask the chrome sufficiently to get additional thickening. That is probably the additional trick here.

Dr. Merrill: Perhaps a few years ago many of you had a call from Dr. Otto, who was in this country and was advocating the use, I think, of sulfaphthalates for pickling. We tried it and did get an enormous increase in thickness yield accompanied by the inevitable decrease in area yield. But we also got a calamitous increase in cracky leather, so we did not carry the experiments very far.

Mr. Lord: In other words, the consensus is that it is difficult to increase the thickness of your leather very much in the tan. I can say, based on some experiments we made which I am not at liberty to discuss, that we do find a considerable difference in area and thickness due to the way we tan our leather. These differences are noted in the shaving room and in the finished leather.

The area yield is not proportional to the thickness yield. In most cases there is a slight loss in measurement. The increase in thickness, however, so far outbalances the decrease in final yield that it does not matter.

Harold Bernard (G. Levor & Company, Gloversville, New York): If you leave the skins in the tannage after 6 or 7 hours—leaving them perhaps in the drum even overnight—you will notice a considerable difference in the thickness of the leather. If you wash them immediately, you will get thinner and flatter leather. But if you leave them overnight in the drum, which is a practice in some cases, you will get plumper and fuller tannage.

MR. LORD: That is because for an additional 12 or 14 hours your skins are continuing to tan, and it is reflected in thickness.

MR. CHAIN: Don't you think if you double the percentage of chrome in your leather, you will get a measurable increase in thickness? Foreign leathers have an increase in thickness, but the break is not as tight as American leather.

DR. BRAUNSCHWEIG: I remember an experiment that I made on various products made in Europe on calfskins, and I found that of all the calfskins which I analyzed (and I believe, if I recall, it was about six or eight), those which were considered the finest in Europe—Traub—had the smallest chrome content in the finished leather—2% to 2½% only. Oppenheimer, also good but not considered the top product, ran as high as 7% or 8%. Freudenberg ran somewhere in between.

So I had, on excellent products, a variation running from as low as 2% to as high as 7% or 8% chrome oxide.

I would like to quote Stiasny in that connection. It does not matter, on a piece of chrome leather, how much chrome you have in your leather. The question is, how it got into the leather.

MR. ZEISSIG: I think from our discussion here that it boils down to one fact: We can vary the chrome and a lot of things, but we don't know one basic thing, and that is, actually, by either physical or chemical tests, what the condition of the fiber is before we start the tanning process. In other words, we don't know just what that collagen is like before we start to tan or to pickle.

We can leave a lime streak or completely delime, we can pickle high or pickle low, we can use masking agents or not, we can even change the amount of chrome from 2% or 3% to 7% or 8%, yet the leathers are pretty close to one another.

If we could find out by physical and chemical means what the condition of that fiber is before we start—one beamhouse will give you a certain fiber and another beamhouse will give you another—if we knew the fiber condition, we could determine what to do later on.

MR. LORD: If you change your process, your white weight changes. If you tan on a white-weight basis, then your tans are entirely different in two cases because, for the amount of hide substance in one case, you have a lot more tan. If you don't take this into account, you can find a difference in your tans.

MR. ZEISSIG: I think we don't know what condition that fiber is in, regardless of the tan. We don't know what it is like chemically.

MR. LORD: That is very true. We know something of the degree of swelling by comparisons and that is all.

MR. ZEISSIG: Yes, but we don't know the condition of the fiber; we are actually guessing.

DR. TURLEY: I think we are kidding ourselves also, if we say we know the degree of swelling. We don't. We only have a vague idea.

MR. LORD: We have a measurable idea of the amount of swelling by the white weight. Whether this is right or wrong, we don't know. But at least we have a measure.

DR. TURLEY: All of this is pointing up what I tried to bring out in earlier papers about this balance of things. You can see two leathers that are sold competitively and made in entirely different ways. You can have a beaming condition which gives a swelling at a particular stage, and you can maintain that in the pickle and have a relatively light tanning. Or you can have a flatter, less plump condition prior to tannage and come out of tannage with leathers that are somewhat similar and that sell competitively. Yet if you look at them closely, you can see the fine points and interesting little differences.

So when you raise this question of how far you can go in plumping with chrome, I will stick my neck out now. The trouble with leather, you know, is that there are no absolute standards. But if you take an ordinary simple process, a well-bated stock, a simple tannage, and not too much chrome, I venture to say that you can make a leather at least 50% thicker by attention to the tannage itself—change in basicity and change in amount, and getting it well beyond the leathering point—and if that is not enough, carrying into the tannage the fullness that comes with beaming.

Many chrome leathers made years ago were full and round, and they were practically tanned on a limed skin. But you will have troubles with uniformity that another tanner won't have. You cannot, according to my experience, delime or leave a constant streak in those hides. They vary in their nature, vary in their substance, and in their thickness. All right, you achieve something. But if you can further work them, take all the lime out, and modify the tannage to bring it back where it was, then you will have less problems of uniformity as to feel and roundness in the leather.

After all, gentlemen, there are a thousand ways to chrome-tan.

MR. ZEISSIG: Dr. Turley, don't you think that you could reach equilibrium if you took all your lime out? It would be fine, but it has been proved in practice that it is better in a lot of cases to leave a little streak. We get a better result—a fuller piece of leather and more of what we are shooting for. If we took that same "piece" of leather and delimed completely, we might be in trouble.

DR. TURLEY: I agree completely. That is what I am trying to point out. Under the condition I have set out, you will attend to that. If you have to delime all you have, then change the tannage in some respect to compensate for that. And then when you work that out and have it under control, you will have a more uniform production, because this so-called lime streak can vary 100% in my judgment even if it is only 15% in the hide (it can vary from 10% to 20%). I have tried in papers to bring that out. Of course, you cannot change one step without producing something undesirable in a piece of leather. You have to compensate for it at some other stage.

Immediately, the most interesting thing that a leather maker can do in connection with his tannery is to see how different tanners compensate for this effect in different ways. It is fascinating as a piece of work.

MR. WILSON: Here are two observations from the thickness standpoint. I doubt whether you will get solid answers from the side leather tanners because of them. First of all, if you consider the list price structure of side leathers and also work under the assumption that, let us say, for a 5% increase in thickness, there will be a corresponding 5% decrease in area, then it is not worthwhile for the side leather tanner to make it thicker and smaller, just by the nature of the list price structure.

The second thing is that for the last six or seven years we have experienced a phenomenon in the meat field which has caused us to buy increasingly thicker hides to make the same thickness leathers. So it is not really an incentive for us.

I. LEO RIESE (Beggs & Cobb): I would like to disagree. I think it is a tremendous incentive, whether it is in the calfskin or side leather field, to get all we can out of certain types of skins. I don't think anybody here can buy exactly the type of skin that he wants to buy. You will always find in any lot of hides you buy a certain percentage of lightweight spready stock which you would not like to be there. And if you could possibly decrease the area 30% and increase the thickness 30%, you would thank God.

MR. WILSON: Oh, yes.

MR. RIESE: Now, regarding the other comment about compensating features which Dr. Turley has been speaking about—he mentioned the fact that it is possible with a very heavy lime streak to get an unevenness. That may be true. However, there are other things which tanners have at their disposal; we are not going into retanning now, but there is a point at which they can use other materials to change the variation in the leather. They add something which is not there in certain hides, in order to level out the differences between them. That is why in recent years tanners have gone up to 30% and 40% of extract, for example, which by itself will level out the grains of hides which previously might have been quite different.

I didn't want to bring in retanning, but that is one means of compensating, so to speak.

CHAIRMAN HENRICH: I think what everybody would like would be to get the thickness without that loss in measurement.

MR. WILSON: We will take both, if we can get them.

DR. SALAMATOV: Do you lose some strength?

MR. LORD: Always.

MR. CHAIN: What is the difference between a one-third lime streak on a lime-split side and one-third lime streak on a side that will be tanned and split in the blue?

CHAIRMAN HENRICH: I guess we have no experience on that.

MR. RIESE: My experience—I may be wrong—is that on sides that are lime-split for the normal 4 or 4½ ounce finished-weight level, it is a pretty good trick if you can keep the third of a lime streak in a lime-split side. I have found if you try to decrease the ammonium sulfate in some way to leave a lime streak in a lime-split side, you still have a uniform pH through that leather, but the pH may be up around 9½ or 10.

I have found it practically impossible to regulate the depth of deliming in a lime-split side the way you can in a side which is not lime-split, because of the difference in the thickness. You get a much quicker equilibrium of your deliming, even if you use very little deliming agent on a lime-split side.

DR. THOMAS THORSTENSEN: The thought just occurred to me on the question of the lime streak that we are something like the bumblebee who theoretically can't fly but flies anyway.

When we are tanning a thick, heavy piece of leather and have a lime streak

in it, we know that as we start to delime and pickle, the lime streak in the hide is not going to be the same over the entire area of the hide. Down in the belly area there will be practically no lime streak, but in the heavy sections of the bends there will be a heavy lime streak.

When the chrome is added, the lime sucks in the chrome, you might say for the lack of a better explanation, because of the higher pH in the center in the thick areas of the hide, driving the chrome tannage inside. We get a good penetration in the heavier areas. This would work as something of a self-compensating effect which should give a fairly even tannage in spite of the lime streak, because it compensates for the thickness in the hide. This is just the opposite effect that we would have in the lime-split stock where we would want a fairly even pH all the way through to have uniformity.

CHAIRMAN HENRICH: For instance, if your leather ordinarily had 4% chrome on a hide-substance basis, and you changed your tannage to give 6% chrome on a hide-substance basis, how much of an increase in thickness would you expect? Is there anybody here who has had experience along those lines?

DR. PANEPINTO: I did just that with some goatskins, but I didn't measure their thickness. What I did was to look at the finished leather, and that had a high grain. It was very, very stretchy.

DR. H. DOBERTHIEN (John A. Lang & Sons): I had an experience we were not looking for. We have our tan made up in barrels the day before. One morning we got a new tanner in, and he measured the tan liquor out to what he thought was a gallon, but it was two. He put twice as much in, so instead of getting about 7% chrome in this particular half-day's work, we got about 14% chrome. This leather went through for a garment. We did get about half again as much weight out of that leather. Mind you, we split it down, and it was the best leather we ever made as far as softness went, but it was heavier on account of the increased chrome.

CHAIRMAN HENRICH: How about your yield?

DR. DOBERTHIEN: I could not see that there was too much difference, as it was cut down to garment weight. It was cut down to 2½ or 3-ounce weight. We were not making side leather out of it.

DR. MERRILL: I do think that increasing the chrome in the leather does increase the thickness yield, but not very much. I cannot be more specific as to what percentage increase in weight you get per extra percent of chrome

oxide, but I would say that going from 4% to 6% or 7% on the hide-substance basis, the difference in thickness is appreciable and worthwhile.

CHAIRMAN HENRICH: One other question along that line: Is it better to try and increase your chrome to that point in the original tan, or would it be better to put in your usual amount of chrome—say 4% or 4½% on a hide-substance basis—and then after splitting and shaving, give it a chrome retan to bring it up to 6½%? What do you feel your effect would be there?

MR. SALAMATOV: We have done that, and it does increase the thickness—not very much, but it definitely helps. I think that question was discussed some time ago, and I think that people from Gallun also had the same experience.

CHAIRMAN HENRICH: Then we might ask, as far as retan is concerned: Is it better to have it a one-bath retan or a two-bath retan? Here is a chance for a little argument. In some of my experiences I have used both. I think possibly with the two-bath retan you get a more uniform chrome distribution throughout the skin than you do in a one-bath retan, but that could be open for discussion.

MR. SALAMATOV: It looks very good before you glaze it. But after you glaze it, I don't want to look at it.

CHET ELLIS (Columbus, Ohio): We ran up against a stumbling block that the side people would not have. It seems that when we add enough to do much good—and we have to add a lot to be noticeable—that after we glaze, we don't get the brightness that we get with less chrome. I think there must be an answer to it and some way to get around it, but we have not accomplished it. If anybody has any theoretical reason why it might be true or some practical way of explaining it, we would like to hear it. We have been able to plump ½ oz. onto a 2-oz. skin, but that is by really piling the chrome in. But then the grain evidently loses its shelliness and does not want to glaze. It will glaze but not as well.

CHAIRMAN HENRICH: In other words, you get a higher grain rather than a nice flat grain?

MR. ELLIS: Just looking at it, it looks pretty good, but the brilliance is not there. That is the main point.

MR. SALAMATOV: I would hazard an explanation this way: You get more chrome on the surface; therefore, your finish does not take on, and you don't get the brightness.

MR. BERNARD: Commenting on that—on various types of retanning with chrome that I have had experience with over the years, you get more plumpness, and with it more coarseness of the grain. It must be that the grain is plumped along with the fiber.

If you want smooth leather, retanning is not the answer as a rule. In making crushed leathers we found retanning gave us the plumper and coarser grain we wanted. If we wanted a smooth, fine grain for glazed kid or a smooth grain in calf, it worked against a smooth grain in every case. But we did get considerable plumping, and I have used it as far back as 1913 on glazed horse fronts where Dr. Merrill worked. We noticed a considerable difference as far back as that in the plumping of retanning with chrome. The leather was much plumper and stood up fairly well with the retannage, but the grain was coarser.

CHAIRMAN HENRICH: What effect did it have on the break of the leather?

MR. BERNARD: In the different types of leather it had a different effect. In the crushed leathers we used a lot of vegetable extract along with the chrome retan. On some of the goatskins, which are apt to be a little bony in spots, it would correct the "cockly" condition which we did not correct with the extract alone. You usually have to adjust your fatliquor or something else because you are really tanning the leather softer and need a fatliquor correction because of that. The break was fair.

But if anybody wants plump leather and can stand the additional coarseness, it certainly does plump. It may not plump as much as some of the wood extracts, but it does plump. That I will say.

DAVID SMALL (Brezner Tanning Corporation, Penacook, New Hampshire): I would like to inject a totally different viewpoint on the question of thickness. From the outlook of the split tanner who is really outside of so much of this discussion because of the lack of grain structure, certainly there is little disagreement with the statement that to the split tanner thickness is perhaps as important as to anybody, if not more so. It has been my experience that although the plumping action that has been referred to here may exist, trying all sorts of variables including most of those that have been mentioned here, it has never been my experience that we could take a split and change the thickness sufficiently to change from one measurable, gaugeable weight category into another higher-priced measurable weight category. You start out with splits that are flimsy, lightweight, with a nogginess, and

end up with a lightweight ooze. You can't make them into a sole leather that would be of much greater value. If we could do it, we would do it with all of our leather, and we can't even come close.

THOMAS BLAIR (Saxe Cutch Corporation, New York): It occurs to me that I saw some work done on an experimental basis using sodium sulfite as a masking agent. If I remember, it was on goatskin, and we got an increase of ½ oz. to 1 oz. on 3-oz. stock without any reduction in strength, using the sodium sulfite before the chrome.

Another item on thickness—this goes back a way, and I may be a little vague on it—but it came to me when there was a remark that someone made about leather made in Europe where the very large lime streak was left in the leather after the pickling. I was exposed to a process of that nature on side leather where the pickling was actually superficial. I don't recall the bate, but it seems to me it was normal. We got a very thick piece of leather. There were some disadvantages. As I remember, it caused a severe grain-cracking situation on certain types of stock that seemed to be particularly tight and heavy. If I remember, the leather was very smooth, but there seemed to be an area reduction along with it, although I don't think that was ever evaluated. It did make very nice leather, and I think that the pickling was somewhere between 3.6 and 3.8 at the end, using a 33% basic chrome tan adjusted with alkali (I don't remember exactly how much) so that we ended up with a pH around 4. I think we added an eighth of a percent of sodium bicarbonate to set the tan.

Would there be any comments on the use of sodium sulfite for masking?

DR. TURLEY: I have had a limited experience with that or seeing it being used. I think your observations are explained by the fact that the sodium bisulfite will automatically adjust the pickle which is given at approximately pH 3½. That will automatically give a little denser structure to the skins, and from there on you can proceed with the chrome tannage. There was a product put on the market which consisted chiefly of sodium bisulfite with a little sodium phthalate, and it was entirely a question of buffering at that pH range.

CHAIRMAN HENRICH: Gentlemen, if there are no further questions, I want to thank you for coming in this morning and the panel for helping us.